

PATENT SPECIFICATION

Best Available Copy

798,604



Date of Application and filing Complete Specification: June 5, 1956.

No. 17362/56.

Application made in United States of America on June 10, 1955.

Complete Specification Published: July 23, 1958.

Index at acceptance:—Classes 2(2), F(1B2: 2D2: 2G); 2(5), R3C(2: 4: 6: 8: 9: 12: 17), R7C(4: 6: 8: 9: 12: 17), R7T2, R22C(4: 6: 8: 9: 12: 17), R22T2, R27K1B, R27K1C(4: 6: 8: 9: 12: 17), R27K3C(4: 6: 8: 9: 12: 17), R27K3M(5: 6: 7); and 2(6), P2A, P2C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P2(D1A: K8), P2T(2A: 2D: 2F), P5A, P5C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P5D2A, P5T(2A: 2D: 2X), P7A, P7C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P7D(1A: 1B: 1X: 2A1: 2A2B), P7K(8: 9: 11), P7T(2A: 2D: 2E: 2F: 2G: 2X), P8A, P8C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P8D(1A: 1B: 2B2: 4), P8K(2: 4: 7: 8: 9), P8T(2A: 2D: 2F), P9A, P9C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P9D(1A1: 1X), P9K(4: 7: 8: 10), P9T(2A: 2D: 2G), P11A, P11C(2: 6A: 8B: 12A: 12X: 13A: 13C: 20D2), P11D(2A: 2X), P11T(2A: 2D).

International Classification:—C08b, f, g.

COMPLETE SPECIFICATION

Improvements in or relating to Liquid Coating Compositions

We, E. I. DU PONT DE NEMOURS & COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to liquid coating compositions, to articles coated therewith and more especially to water blister-resistant paints for wood and similar substrates permeable to water or water vapour.

Water blistering or moisture blistering is a common form of paint failure especially in paints used on the outside of wood houses. When such failure occurs, blisters develop somewhere between the outer surface of the paint and the wood. These blisters may be as small as a pinhead or as large as a person's hand, sometimes even larger. When they are new, they are full of water. Sometimes they break, and sometimes the water disappears without breaking the film; but in both cases the blistered part of the paint film has lost adhesion and is therefore unserviceable and unsightly or will shortly become so. Repainting is quite costly, largely because the loose paint must be removed; and, if the newly painted surface is to be smooth and uniform the old painted surface must be made uniform, usually by burning and scraping. However, even these elaborate methods do not necessarily solve the problem because frequently the new paint will blister as badly as the old.

The broad object of this invention is to provide liquid coating compositions which resist water blistering when applied to wood and similar water- or water vapour-permeable substrates and articles coated therewith. A further object is to provide such coating compositions of the air-drying oil-base type, i.e. paints and the like in which the organic film-forming material air-dries (dries and hardens at least partly by oxidation) when a thin film or coating is exposed to air at normal atmospheric temperatures, such as linseed oil, gum or resin-containing drying oil varnishes, and drying-oil-modified alkyd resins. A further specific object is to provide air-drying water blister-resistant paints for wood houses or other structures where water blistering is commonly encountered.

According to a feature of the present invention there is provided a liquid coating composition the dry coating of which is characterised by water-blister resistance comprising an air-drying organic film-forming material and a particulate water-insoluble polymeric reaction product of at least one polyanionic linear polymer and at least one polycationic linear polymer combined in substantially chemically equivalent amounts through a plurality of ionic cross-linkages.

In the description of this invention and in the appended claims the term "polyanionic linear polymer" and related terms mean an anionic polyelectrolyte, i.e. a linear polymer the anion of which is polymeric and contains a plurality of lateral substituents having anionic negative charges, for instance polyacrylic acid or sodium polyacrylate. The term "poly-

[Price

cationic linear polymer" and related terms mean a cationic polyelectrolyte, i.e. a linear polymer the cation of which is polymeric and contains a plurality of groups having cationic positive charges, for instance, polymeric poly-quaternary ammonium salts.

Polymers cross-linked through ionic linkages have been described in the literature, e.g. in an article by Fuoss and Sadek, Science, Vol. 110, page 552 (1949). They are obtained by reacting polyanionic polymers with polycationic polymers—in this invention in substantially chemically equivalent amounts, i.e. amounts which provide approximately the same number of anionic negative charges as there are cationic positive charges. The resulting polymeric reaction products are cross-linked through a plurality of ionic linkages and are substantially insoluble in water, as evidenced by the fact that they occur as filterable precipitates when water solutions of appropriate polyanionic and polycationic polymers are admixed.

The particulate water-insoluble polymeric reaction product employed in the compositions of the invention is preferably a reaction product of a polyanionic linear polymer containing a plurality of carboxylic, sulphonic or phosphoric groups or the corresponding salt groups and a polycationic linear polymer containing a plurality of amino, amino addition salt or quaternary ammonium groups.

Suitable polyanionic polymers include polymers of polymerisable aliphatic monocarboxylic acids having a methylene group attached by an ethylenic double bond to a carbon atom *alpha* to the carboxylic acid group, such as polyacrylic acid, polymethacrylic acid, polyethacrylic acid and poly-*alpha*-chloroacrylic acid; copolymers of methacrylic acid or acrylic acid with other polymerisable materials such as methyl methacrylate, vinyl acetate, styrene, 1,3-butadiene, and acrylonitrile; hydrolysed copolymers of *alpha*-*beta* ethylenically unsaturated dicarboxylic acid anhydrides, for example maleic anhydride with polymerisable vinylidene compounds, such as, ethylene, propylene, isobutylene, styrene, vinyl acetate, vinyl chloride, or methyl acrylate; polysulphonic acids, such as polyvinylsulphonic acid; polyphosphoric acids, such as are obtained by reacting *ortho*-phosphoric acid with polymers containing epoxy groups; and polymers, which are derived from naturally occurring materials and which contain a plurality of acidic groups, such as lignic acid, alginic acid, pectinic acid, arabic acid, polygalacturonic acid and carboxymethyl cellulose. Likewise, salts of the above mentioned materials may be used, for instance the sodium, potassium or ammonium salts. The preferred polyanionic linear polymers are the salts of polyacrylic acid.

Suitable polycationic polymers include linear polymers and copolymers containing a

plurality of primary, secondary or tertiary amino groups. Although polymeric quaternary ammonium salts of either *beta*-di-methylaminoethyl methacrylate or *beta*-diethylaminoethyl methacrylate are the preferred polycationic polymers, the acrylate analogues are useful, as well as the copolymers thereof with lower alkyl methacrylates or acrylates. Other representative examples include *beta*-di-*n*-butyl-aminoethylmethacrylate, *beta*-dicyclo-hexylaminoethyl methacrylate, 4-(*beta*-methacryloxyethyl)morpholine, 1-(*beta*-methacryloxyethyl)piperidine, 2-(diethylamino)cyclohexyl methacrylate, triethanolamine monomethacrylate and *beta*-dimethylaminoethylacrylate. Additional examples of suitable polycationic polymers are polyvinyl amines, polyvinylpyridines, polyvinylquinolines, hydrogenated 1,3-butadiene/acrylonitrile and 1,3-butadiene/methacrylonitrile copolymers, polyamines obtained by reductive amination of ethylene/carbon monoxide copolymers, polyethyleneimine, poly-*N*-methylethylenimine, linear polyamides containing intralinear tertiary amino groups, reaction products of vinyl ketone polymers with ammonia or primary amines, polymeric amines resulting from the reaction of ammonia or an amine with a polymer containing epoxy groups. Likewise salts, particularly the quaternary ammonium salts, of the above mentioned materials may be used, such as the acetates, chlorides, sulphates and alkyl sulphates. Other useful quaternary ammonium salts may be prepared by reacting *alpha*, *omega*-dihalides with *N,N,N',N'*-tetraalkyldiamines or by reacting tertiary amines with halogenated polymers such as chlorinated polyvinyl toluene.

The polyanionic and the polycationic polymers may also contain additional functional groups capable of bringing about covalent crosslinking between the two polymers. Such functional groups include, for example, epoxy, hydroxy, mercapto, halogeno, carbalkoxy and amido groups. When such non-ionic functional groups are present, it is desirable that these groups on the polyanionic polymer be reactable with non-ionic functional groups on the polycationic polymer. When the non-ionic functional groups on the polymers are not reactable with each other, covalent-crosslinking may be accomplished by reacting the two polyionic polymers with a polyfunctional reagent having functional groups reactable with the non-ionic functional groups of the two polymers to establish atomic bridges across the polymer chains. Such reagents include, for example, alkylene dihalides, aralkylene dihalides, ethylene oxide, propylene oxide, formaldehyde, dimethylolurea, dimethylolmelamine, dimethylolurons, dimercaptans and glycols.

The desired ion-crosslinked polymers may be prepared in the presence of an inexpensive, inert, finely-divided solid, such as a pigment (e.g. magnesium silicate, whereby it is believed

a thin coating of polymer is developed on the surface of the particles.

Preferred individual water-insoluble polymeric reaction products, for use in the coating compositions of the invention are poly - *beta*-methacryloxyethyl-diethylmethylammonium-polyacrylate, poly-*beta*-methacryloxyethyl-diethylmethylammonium polymetaphosphate, poly - *beta*-methacryloxyethyl-diethylmethylammonium polystyrene sulphate, poly - *beta*-methacryloxyethyl-diethylmethylammonium carboxymethylcellulose and poly-N-methyl-4-vinylpyridinium polyacrylate.

The particulate water-insoluble polymeric reaction product (ion-crosslinked polymer) may be present in the compositions of this invention in any amount which provides the desired degree of improvement in water blister resistance or permeability, usually from 1% to 35%, preferably 3% to 20%, by weight based on the total weight of non-volatile components —i.e. those which do not evaporate when a thin film or coating (e.g. 1—3 mils thick) of a composition of this invention is exposed to the air at normal atmospheric temperature. Below 1%, there is little, if any, beneficial effect. Above 35%, disadvantages usually set in, such as poor durability, high cost, and poor application properties.

Linseed oil and linseed oil modified alkyd resins specified in the Examples which follow illustrate the air-drying organic film-forming materials for use in this invention. However other equivalent materials may be used in other coating compositions made according to this invention or may be used in the Examples in place of all or part of the corresponding material therein. Thus the preferred film-forming materials are the natural glyceride drying and semi-drying oils such as linseed, tung, perilla, soya and oiticica in their natural, refined or bodied forms, alkyd resins modified therewith, and alkyd resins modified with fatty acids derivable from the above drying or semi-drying oils. A preferred range of oil or oil acid content is 50%—80% by weight of the non-volatile solids in said alkyd resin. These alkyd resins can be made from a wide variety of well-known polyhydric alcohols and polybasic acids. Other suitable air-drying film-formers are synthetic esters such as drying or semi-drying oil fatty acid esters of polyhydric alcohols (e.g. pentaerythritol, sorbitol, and the class represented by epichlorohydrin-diphenylolpropane condensates), and gum-containing varnishes based on such synthetic

esters or glyceride oils. Synthetic drying oils, such as certain polymers of butadiene 1,3, are also useful as the film-former.

The coating compositions of the invention may optionally additionally incorporate additives well-known to those skilled in the art, for use in coating compositions such as pigments, solvents or driers. If clear unpigmented products are desired, pigments may be omitted. Likewise driers, bodying agents, surface active agents, inhibitors, colouring matter and the like may be used or omitted, as desired.

In a preferred embodiment of this invention, the water blister-resistant coating composition comprises house paint containing linseed or other drying oil, white and/or coloured pigment, volatile organic solvent, optional additives like driers and a particulate water-insoluble polymeric material as hereinbefore described.

According to a further feature of the invention there is provided an article, especially a wooden article having a dry coating of a coating composition of the invention. The coated articles preferably have a multiple layer dry coating comprising a layer of alkyd resin primer in adherent contact with said article and a layer of a coating composition of the invention in adherent contact with said primer.

The coating compositions of this invention may be applied to the substrate by any of the conventional methods of application such as brushing, roller coating, spraying, knifing or dipping.

Coating compositions of this invention may be used as a single coat finish although, when used on wooden structures like houses, two or three coats are preferred. On new bare wood or on wood from which the old paint has been removed, the preferred first coat or primer is as stated above of an alkyd resin primer of the type described in Example I, and the subsequent coats are preferably of a linseed oil paint of the type prepared in Example I.

Although the coating compositions of this invention are most useful as protective and decorative coatings on the exterior of wooden structures (e.g. white pine, yellow pine, cedar) which are susceptible to water blistering, obviously they may be used on other substrates even where water blistering is not a problem.

The following Examples are provided by way of illustration but not of limitation. Unless otherwise indicated, the parts and percentages are by weight.

EXAMPLE I

Linseed Oil Paint Containing
Ion-Crosslinked Polymer (A)

Part 1		Parts by Weight
5	Linseed Oil	15.35
	Heat Bodied Linseed Oil (Z-2 Gardner-Holdt Viscosity)	11.10
	Titanium Dioxide Pigment	15.20
	Zinc Oxide Pigment	21.80
10	Magnesium Silicate Pigment	11.25
	Ion-Crosslinked Polymer	6.10
	Mineral Spirits	1.80
Part 2		
	Linseed Oil	8.55
15	Lead Naphthenate Drier—16% Pb	2.30
	Manganese Naphthenate Drier—3% Mn	0.16
	Aqueous Ammonium Stearate Solution—1%	0.72
	Mineral Spirits	5.67
		100.00

20 This composition was prepared by grinding the ingredients of Part I in conventional paint grinding equipment to produce a smooth dispersion. Then the ingredients of Part 2 were admixed therewith.

25 The ion-crosslinked polymer was poly-*beta*-methacrylyloxyethyldiethylmethylammonium polyacrylate. It was prepared by mixing an aqueous solution containing 94 parts by weight (one chemical equivalent) of sodium polyacrylate ("Good-Rite" K-710, B. F. Goodrich Chemical Co.) as the poly-anionic linear polymer with an aqueous solution containing 311 parts by weight (one chemical equivalent) of poly-*beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate as the polycationic linear polymer. The ion-crosslinked polymer which precipitated from the aqueous solution was filtered and washed substantially free of sodium methyl sulphate. The recovered precipitate was dried for about 3 days at about 60° C., was reduced to about $\frac{1}{8}$ inch mesh size and was further dried at about 60° C. The polymer was then ground in xylene in a ball mill for about three

days. The milled finely divided polymer was finally separated from the xylene and dried. 45

The ion-crosslinked polymer was present in this paint in the amount of about 6.7% by weight of the non-volatile components (oils, pigments, ion-crosslinked polymer, solid matter in driers, etc.). 50

Prior Art Linseed Oil Paint (B)

For purposes of comparison, an analogous prior art composition was prepared according to the foregoing formula and process except that the ion-crosslinked polymer was omitted and 23.5 parts by weight of magnesium silicate pigment were used in place of the 11.25 parts shown in the formula. 55

Alkyd Resin Primer (C)

For use in priming certain panels for test purposes, a prior art alkyd resin-containing primer for wood structures having the following formula was prepared by well-known means: 60

65

Parts by Weight

Best Available Copy

5	64% linseed oil modified glyceryl phthalate resin (83% solution in aromatic hydrocarbon solvent)	41.9
	Titanium dioxide pigment	39.7
	Soya lecithin solution (10% in mineral spirits)	2.5
	Lead naphthenate drier—16% Pb	1.9
	Manganese naphthenate drier—3% Mn	0.3
10	Creosole inhibitor solution (10% in mineral spirits)	0.5
	Aromatic hydrocarbon solvent	13.2
		100.0

Linseed Oil Primer (D)

- 15 For use in priming certain other panels for test purposes, a prior art linseed oil-containing primer for wood structures having the following formula was prepared by well-known means:

		Parts by Weight
20	Raw linseed oil	6.3
	Bodied linseed oil (83% solution in mineral spirits, Gardner-Holdt viscosity U—W)	12.5
	Titanium dioxide pigment	10.5
25	Basic carbonate white lead pigment (84.5% in linseed oil)	15.6
	Magnesium silicate pigment	32.8
	Lead naphthenate drier—16% Pb	1.7
30	Manganese naphthenate drier—3% Mn	0.3
	Mineral spirits	20.3
		100.0

The above described products were used in a testing programme to determine the water blister resistance of the linseed oil paint containing ion-crosslinked polymer in comparison with the prior art linseed oil paint.

In this test duplicate Western red cedar boards ($\frac{3}{8} \times 6 \times 36$ inches) was painted on one side with two or three coats, each about 1.5—2 mils thick when dry, of various combinations

of these products as indicated in the following Table I. The coatings were dried by exposure to air at room temperature, and the panels were exposed to outdoor weather for two months on a vertical fence facing south.

The weathered test boards were then subjected to an accelerated water blister test in which the painted side of the board was in contact with a controlled atmosphere main-

tained at a constant temperature of about 35° F. and a constant relative humidity of about 40%. The unpainted side was in contact with a controlled atmosphere maintained at about 70° F. and 70% relative humidity. The

painted sides were examined periodically for 30 days to determine whether blisters had developed and, if so, how many and how big they were.

The results are recorded in the following

table, in which "excellent" means at most only a few scattered blisters of very limited size, e.g. 1/8 inch across, and "poor" means many blisters ranging in size from silver-half dollar to the area of a man's hand or even larger.

TABLE I

WATER BLISTER RESISTANCE OF PAINTED WOOD

	Board Number											
	1	2	3	4	5	6	7	8	9	10	11	12
First Coat												
New Paint A	—	—	—	—	x	—	—	—	—	—	x	—
Prior Art Paint B	—	—	—	—	—	x	—	—	—	—	—	x
Alkyd Primer C	x	x	—	—	—	—	x	x	—	—	—	—
Linseed Oil Primer D	—	—	x	x	—	—	—	—	x	x	—	—
Second Coat												
New Paint A	x	—	x	—	x	—	x	—	x	—	x	—
Prior Art Paint B	—	x	—	x	—	x	—	x	—	x	—	x
Third Coat												
New Paint A	x	—	x	—	x	—	none	none	none	none	none	none
Prior Art Paint B	—	x	—	x	—	x	"	"	"	"	"	"
Resistance to Water Blistering	Excellent	Good	Excellent	Good	Fair	Poor	Excellent	Good	Excellent	Good	Fair	Poor

It will be seen from these results that, in each comparison, the new Paint A containing ion-crosslinked polymer was superior in water blister resistance to the prior art (Paint B). The superiority of paint containing ion-crosslinked polymer was confirmed in large scale tests in-

volving the painting of several wooden houses known to have paint blistering histories. It was also determined in these large scale tests that paint containing ion-crosslinked polymer had application properties, durability and appearance retention properties substantially equal to

analogous paints containing no ion-crosslinked polymer.

In further laboratory tests designed to measure water-vapour permeability of paint films (see "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and

Colors" by Gardner and Sward), it was determined that films containing the ion-crosslinked polymer were 2—4 times as permeable to water vapour as analogous paint films containing no ion-crosslinked polymer.

In additional blistering and permeability tests, paints identical in composition to Paint A, except that the amount of ion-crosslinked polymer was varied between 1% and 35% by weight of the non-volatile components, were prepared and found to be water blister resistant and permeable, in comparison with Paint A, substantially in proportion to the amount of ion-crosslinked polymer present.

Examples II—VII. Improvements in water blister resistance and permeability substantially equivalent to those described in Example I were obtained in paints prepared as in that Example except for substituting the following ion-crosslinked polymers for the corresponding polymer in Example I on an equal weight basis.

EXAMPLE II

Poly - *beta* - methacrylyloxyethyldiethylmethylammonium polymetaphosphate, prepared from chemically equivalent amounts of potassium polymetaphosphate (see Iler, J. Phys. Chem. 56, 1086—1089 (1952)) and poly *beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate.

EXAMPLE III

Poly-*beta*-methacrylyloxyethyldiethylmethylammonium polystyrene sulphonate, prepared from chemically equivalent amounts of potassium polystyrene sulphonate and poly *beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate.

EXAMPLE IV

Poly-*beta*-methacrylyloxyethyldiethylmethylammonium carboxymethyl cellulose, prepared from chemically equivalent amounts of sodium carboxymethyl cellulose and poly - *beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate.

EXAMPLE V

Poly-*beta*-methacrylyloxyethyldiethylmethylammonium alginate, prepared from chemically equivalent amounts of sodium alginate ("Kel-tex," Kelco Co.) and poly-*beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate.

EXAMPLE VI

Poly-N-methyl - 4 - vinylpyridinium polyacrylate, prepared from chemically equivalent amounts of sodium polyacrylate and poly-N-methyl-4-vinylpyridinium methyl sulphate.

EXAMPLE VII

Poly-*beta*-methacrylyloxyethyldiethylmethylammonium polyacrylate/polyphosphate, prepared from chemically equivalent amounts of (a) a 50:50 mixture of sodium polyacrylate and potassium polymetaphosphate and (b) poly - *beta*-methacrylyloxyethyldiethylmethylammonium methyl sulphate.

EXAMPLE VIII

The following is a formula for an alkyl resin paint for wood structures, containing about 13.7% ion-crosslinked polymer by weight based on the total non-volatile components and having improved water blister resistance and water vapour permeability.

Parts by Weight

75	64% linseed oil modified glyceryl phthalate resin (83% solution in aromatic hydrocarbon solvent)	37.90
	Titanium dioxide pigment	24.70
	Antimony oxide pigment	2.50
	Ion-crosslinked polymer (same as used in Example I)	9.60
80	Soya lecithin solution (10% in mineral spirits)	1.30
	Creosole inhibitor solution (10% in mineral spirits)	0.35
	Lead-manganese drier	3.55
85	Aqueous ammonium stearate solution—1%	1.00
	Aromatic hydrocarbon solvent	19.10
		<u>100.00</u>

This composition was prepared by the process disclosed in Example I, by grinding the pigments and the ion-crosslinked polymer with part of the liquid ingredients and subsequently admixing the resulting dispersion with the other ingredients.

Other similar compositions may be made by substituting 1%—35% of the same or other ion-crosslinked polymers for the 13.7% used in this Example, the percentages being based on the total weight of non-volatile components.

What we claim is:—

1. A liquid coating composition the dry coating of which is characterised by water-blister resistance comprising an air-drying organic film-forming material and a particulate water-insoluble polymeric reaction product of at least one polyanionic linear polymer, as hereinbefore defined, and at least one polycationic linear polymer as hereinbefore defined, combined in substantially chemically equivalent amounts through a plurality of ionic cross-linkages.

2. A coating composition as claimed in claim 1 in which the particulate water-insoluble polymeric reaction product is a reaction product of a polyanionic linear polymer containing a plurality of carboxylic, sulphonic or phosphoric groups or the corresponding salt groups, and a polycationic linear polymer containing a plurality of amino, amino addition salt or quaternary ammonium groups.

3. A coating composition as claimed in claim 1 or 2 in which the polyanionic linear polymer is a salt of polyacrylic acid.

4. A coating composition as claimed in any one of the preceding claims in which the polycationic linear polymer is a polymeric quaternary ammonium salt of either *beta*-dimethylaminoethyl methacrylate or *beta*-diethylaminoethyl methacrylate.

5. A coating composition as claimed in claim 1 in which the particulate water-insoluble polymeric reaction product comprises poly-*beta*-methacrylyloxyethyldiethylmethylammonium polyacrylate.

6. A coating composition as claimed in claim 1 in which the particulate water-insoluble polymeric reaction product comprises poly-*beta*-methacrylyloxyethyldiethylmethylammonium polymetaphosphate.

7. A coating composition as claimed in claim 1 in which the particulate water-insoluble polymeric reaction product comprises poly-*beta*-methacrylyloxyethyldiethylmethylammonium polystyrene sulphonate.

8. A coating composition as claimed in claim 1 in which the particulate water-

insoluble polymeric reaction product comprises poly-*beta*-methacrylyloxyethyldiethylmethylammonium carboxymethylcellulose.

9. A coating composition as claimed in claim 1 in which the particulate water-insoluble polymeric reaction product comprises poly-N-methyl-4-vinylpyridinium polyacrylate.

10. A coating composition as claimed in any one of the preceding claims in which the particulate water-insoluble polymeric reaction product is present in an amount of from 1% to 35% by weight based on the total weight of non-volatile components.

11. A coating composition as claimed in any one of the preceding claims in which the particulate water-insoluble polymeric reaction product is present in an amount of from 3% to 20% by weight based on the total weight of non-volatile components.

12. A coating composition as claimed in any one of the preceding claims in which the air-drying organic film-forming material comprises a glyceride drying or semi-drying oil.

13. A coating composition as claimed in any one of claims 1 to 12 in which the air-drying organic film-forming material comprises an alkyd resin modified with a glyceride drying or semi-drying oil or fatty acid derivable from a glyceride drying or semi-drying oil.

14. A coating composition as claimed in claim 13 in which the modified alkyd resin contains oil or oil acid in an amount of from 50% to 80% by weight of the non-volatile solids in said alkyd resin.

15. A coating composition as claimed in any one of the preceding claims which additionally incorporates additives such as pigments, solvents or driers.

16. A coating composition as claimed in any one of the preceding claims when prepared substantially as described in the foregoing Examples.

17. An article, especially a wooden article, having a dry coating of a coating composition as claimed in any one of the preceding claims.

18. An article as claimed in claim 17 having a multiple layer dry coating comprising a layer of alkyd resin primer in adherent contact with said article and a layer of a coating composition as claimed in any one of claims 1 to 16 in adherent contact with said primer.

19. An article as claimed in claim 17 or 18 when prepared substantially as described in the foregoing Examples.

For the Applicants:

J. A. KEMP & CO.,
Chartered Patent Agents,
8—10 Staple Inn, London, W.C.1.